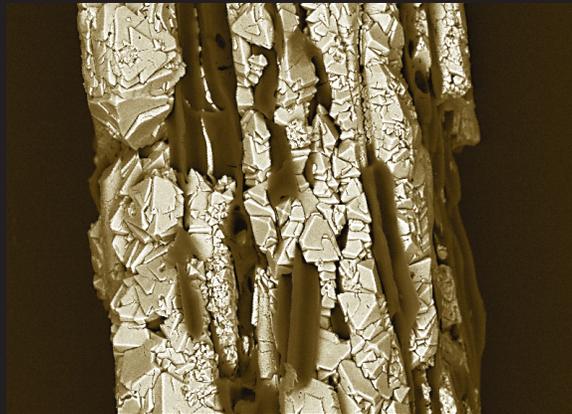


Heavy Minerals and Sedimentary Organic Matter in Pleistocene and Cretaceous Sediments on Long Island, New York, with Emphasis on Pyrite and Marcasite in the Magothy Aquifer

U.S. GEOLOGICAL SURVEY

Water Resources Investigations Report 99-4216



Heavy Minerals and Sedimentary Organic Matter in Pleistocene and Cretaceous Sediments on Long Island, New York, with Emphasis on Pyrite and Marcasite in the Magothy Aquifer

By Craig J. Brown, John Rakovan, and Martin A.A. Schoonen

U.S. GEOLOGICAL SURVEY
Water-Resources Investigations Report 99-4216

Prepared in cooperation with the
SUFFOLK COUNTY WATER AUTHORITY



Coram, New York
2000

U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. Geological Survey
Charles G. Groat, Director

The use of firm, trade, and brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey

For additional information
write to:
U.S. Geological Survey
2045 Route 112, Bldg. 4
Coram, NY 11727

Copies of this report may be purchased from:
U.S. Geological Survey
Branch of Information Services
Box 25286
Denver, CO 80225-0286

CONTENTS

Abstract	1
Introduction	2
Purpose and scope	3
Previous heavy-mineral studies	3
Study methods	5
Borehole sampling	5
Laboratory analyses	5
Geologic framework of Long Island	6
Heavy minerals and sedimentary organic matter	8
Vertical variations	8
Lateral variations	8
Grain size	12
Pyrite and marcasite in the Magothy aquifer	12
Mineralogic and lithologic description of selected	13
Landscape Drive cores	13
Adams Avenue cores	13
Locust Drive cores	14
Margin Drive cores	14
Moriches-Riverhead Road cores and Scuttlehole Road cores	16
Mineral reactivity	16
Summary and conclusions	20
References cited	20

FIGURES

1. Map of Long Island, N.Y., showing locations of the borehole sites and line of section A-A' along Nassau-Suffolk County border, Long Island, N.Y.	3
2. Hydrologic section A-A' along the Nassau-Suffolk County border, showing projections of nearby boreholes studied in this report	4
3. Photographs of lignite from the Magothy aquifer, Long Island: A. laminae or thin beds in split-spoon core sample. B. Lignite "wood" pieces from site LO. C. Secondary electron image of lignite wood cells from site AD.....	10
4. Plots showing abundance of (A) silt and clay, and (B) total sulfur and organic carbon, in core-sample sediments relative to altitude below sea level, and log percent (C) total sulfur and D) silt and clay, as a function of log organic carbon percentage of core samples from borehole S79407T, Suffolk County	11
5. Photographs of pyrite and marcasite from the Magothy aquifer in Suffolk County: A. pyrite crystals within lignite from site LO. B. pyrite crystals in a spheroid aggregate from site SC. C. Interstitial marcasite in quartz sand from site AD.....	13
6. Scanning-electron microscope images showing etched octahedral pyrite crystals from site LA, Suffolk County: A. Random etchings. B. Localized etching	14

7. Scanning-electron microscope images of iron-sulfide minerals from site AD, Suffolk County: A. Etched octahedral pyrite crystals, B. Interstitial marcasite cement. (C) Platey marcasite crystals in marcasite cement. D. Parallel growth steps, of platey marcasite. E. Cockscomb marcasite	15
8. Scanning-electron microscope images of samples from site LO, Suffolk County: A. Pyrite crystals and lignite wood-cell structures. B. Octahedral pyrite crystals	16
9. Scanning-electron microscope images of samples from site MA near the southern shore of Suffolk County: A. Cockscomb-growth marcasite crystals overgrown with smaller crystals of octahedral pyrite. B. Cubo-octahedral pyrite crystals. C. Framboidal pyrite. D. Octahedral pyrite on lignite. E. Cubo-octahedral pyrite. F. Glauconite.	17
10. Scanning-electron microscope image showing poorly crystalline marcasite cement with stalactite-shaped crystals from site MO, Suffolk County	18
11. Cubic pyrite from site SC, Suffolk County: A. "Ball," about 1 centimeter in diameter. B. Interlocking cubic {100} crystals on surface of ball; C. Thin section of "ball" showing wedge-shaped crystals radiating the center. Arrows near center indicate lenticular lignite pieces. D. Magnified image showing the internal radial texture	18
12. Wavelength-dispersive maps showing the distribution of selected elements (as indicated by light color) associated with iron-bearing minerals and rutile among quartz grains, surrounded by pyrite cement in sample from site MA, Suffolk County, at 117 m below sea level.....	19

TABLES

1. Altitudes, hydrogeologic units, and methods of analysis for borehole samples from Nassau and Suffolk Counties, Long Island	7
2. Most abundant heavy minerals in sand-size fractions in borehole cores from Nassau and Suffolk Counties, Long Island	9

CONVERSION FACTORS, ABBREVIATIONS AND VERTICAL DATUM

Multiply	By	To Obtain
<i>Length</i>		
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
<i>Area</i>		
<i>Chemical Concentration</i>		
	milligram per liter (mg/L)	
	micromoles per gram ($\mu\text{mol/g}$)	
	grams per cubic centimeter (g/cm^3)	
<i>Other abbreviations used</i>		
	less than (<)	
	greater than (>)	

Vertical datum: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Heavy Minerals and Sedimentary Organic Matter in Pleistocene and Cretaceous Sediments on Long Island, New York, with Emphasis on Pyrite and Marcasite in the Magothy Aquifer

by Craig J. Brown¹, John Rakovan², and Martin A.A. Schoonen^{3,4}

ABSTRACT

Abundance and distribution of iron-bearing and other heavy minerals in sediments of Long Island, N.Y., were examined to identify sources and sinks of dissolved iron and other ground-water constituents along a deep flow path from the ground-water divide to the southern shore along the Nassau-Suffolk County border. The occurrence and reactivity of many iron-bearing minerals in the aquifer system are affected by terminal electron-accepting processes, which are a function of depth below land surface, distance from the ground-water divide, and organic-matter content of the sediment. The lateral distribution of heavy minerals within lithologic sediments is not uniform throughout Long Island, or even along the 30-kilometer study section at the Nassau-Suffolk County border. Mineralogy and mineral abundance in Pleistocene units differ from those in Cretaceous sediments, and some of the trends vary with depth as well as from north to south.

Major heavy minerals in the Cretaceous sediments at the study sites include pyrite, marcasite, muscovite, leucoxene, ilmenite, rutile, stau-

rolite, chloritoid, and aluminosilicates (Al_2SiO_5); those in the overlying Pleistocene deposits at one site include iron oxides, leucoxene, zircon, garnet, ilmenite, aluminosilicates, and hornblende. Pyrite, marcasite, garnet, hornblende, and tourmaline were found locally in the Cretaceous sediments. Pyrite and marcasite were detected less frequently in borehole samples from near the ground-water divide, where the ground water is generally oxic, than in those from near the southern shore of Long Island, but were found in sulfate-reducing zones throughout the Magothy aquifer. Glauconite was present in Cretaceous and Pleistocene deposits, but only in the marine or transitional units. The most abundant and potentially reactive of the iron-bearing minerals found were iron (hydr)oxides, leucoxene, glauconite, chlorite, pyrite, and marcasite.

The presence and morphology of pyrite and marcasite can be indicative of the microbial and geochemical environments. Pyrite generally was found in association with lignite or as interstitial cement. Marcasite was found as interstitial cement and is associated with the oxidation of iron-sulfide minerals upgradient. Pyrite crystals were octahedral, cubic, cubooctahedral, and framboidal, and many samples showed more than one generation of crystal growth. Marcasite cement, which consisted of platy crystals in most samples, probably forms only under nonmarine conditions.

¹U.S. Geological Survey, 2045 Route 112, Coram, NY 11727

²Department of Geology, Miami University, Oxford, OH 45056

³Department of Geosciences, SUNY-Stony Brook, Stony Brook, NY 11790

⁴Long Island Groundwater Research Institute, SUNY-Stony Brook, Stony Brook, NY 11790

INTRODUCTION

High concentrations of dissolved iron (> 0.5 mg/L) in ground water contribute to the biofouling of public-supply wells, for which treatment and remediation is costly (Walter, 1997). The distribution of iron-bearing minerals and other heavy minerals⁵ within an aquifer affects the concentrations of iron and other dissolved constituents at any given location along a ground-water flow path. The abundance and reactivity of many heavy minerals are affected by terminal electron-accepting processes (TEAPs), which are a function of the depth below land surface, the distance from the ground-water divide, and the sedimentary organic matter (SOM) content of the surrounding material. The predominant TEAPs in the Magothy aquifer (the principal source of water supply on Long Island, N.Y.) include microbially mediated O₂ reduction, Fe(III) reduction, and sulfate reduction (Brown and others, 1999b). Iron hydr(oxides), for example, are more stable in oxic zones of the aquifer than in anoxic zones, and generally undergo reduction through iron-reducing or sulfate-reducing TEAPs (Lovley, 1987; Coleman and others, 1993).

The morphology and texture of iron-sulfide minerals (pyrite and marcasite) also are affected by the chemical composition of adjacent sediments and pore water (Raiswell, 1982). For example, the various textural phases of pyrite are the result of factors that affect (1) the rate and magnitude of sulfate reduction (such as sulfate availability, presence of sulfate-reducing bacteria, and concentration of metabolizable organic matter), and (2) the extent of iron sulfide supersaturation (such as the sulfide concentration in pore water and the availability of local reactive iron) (Raiswell, 1982). The formation of framboidal⁶ pyrite probably requires local sources of reactive iron that are transported small distances by diffusion to zones of sulfate reduction, whereas the formation of euhedral⁷ pyrite requires transport of iron from adjacent horizons (Raiswell, 1982). Ground-water pH also affects morphology—pore water with a pH below 5 would favor the precipitation of marcasite rather than pyrite (Murowchick and Barnes, 1986), although a pH

⁵Minerals with a high density (> 2.7 g/cm³) that are separated in the laboratory from minerals of lower density by means of heavy liquids, such as bromoform.

⁶Aggregates of tiny spherical particles.

⁷Crystals completely bounded by regularly developed crystal faces.

below 3 could impede microbial processes that affect iron and sulfur transformation (Chapelle, 1993).

Identification of the geochemical reactions that affect the dissolved iron concentrations in the Long Island aquifer system requires study of the reactive minerals and the organic carbon content of the sediments. The low dissolved-solids concentration of Long Island ground water reflects the paucity of reactive minerals in the sediments that form the major aquifers (Pearson and Friedman, 1970). These sediments consist mostly of quartz sand, and the heavy-mineral component generally constitutes less than a few percent by weight. Iron, which is one of the most reactive dissolved constituents of Long Island ground water (Brown and Schoonen, 1994), is derived from (1) iron coatings on sediment grains, (2) the heavy-mineral fraction of sediment grains, and (3) oxidation of authigenic iron-sulfide minerals (Brown and others, 1999a). Iron-sulfide minerals (pyrite and marcasite) form in sulfate-reducing zones of the Magothy aquifer, but are oxidized as lignite becomes depleted by weathering, and redox conditions become oxic (Brown and others, 1999a). The heavy minerals in the sediments on Long Island are derived mainly from weathered crystalline and metamorphic rocks of New York and New England (Perlmutter and Todd, 1965) but also include authigenic minerals such as pyrite, marcasite, and glauconite (Brown and others, 1998).

The abundance of heavy minerals and sedimentary organic carbon in Long Island sediments has been studied by several workers (see “Previous Studies” section), but the spatial distribution of these minerals has not been examined in detail. This information is needed for geochemical modeling and the study of iron geochemistry along ground-water flow paths.

In 1994, the U.S. Geological Survey (USGS), in cooperation with the Suffolk County Water Authority (SCWA), began a study of iron geochemistry and chemical evolution of ground water along a flow path from the ground-water divide near the Nassau-Suffolk County border to the southern shore (fig. 1). The initial phase of the study included delineation of heavy-minerals distribution in the upper Cretaceous deposits, including the Magothy aquifer, and in the saturated part of the overlying Pleistocene deposits (upper glacial aquifer). Heavy minerals from core samples collected near the ground-water divide (the area of Magothy recharge) were studied and compared with

mineralogical data from previous studies elsewhere in Nassau and Suffolk Counties to help define the geochemical reactions along the flow path (fig. 2). An analysis of iron-sulfide minerals and SOM content of the aquifer material obtained from six Magothy boreholes during the SCWA drilling program was included in this study.

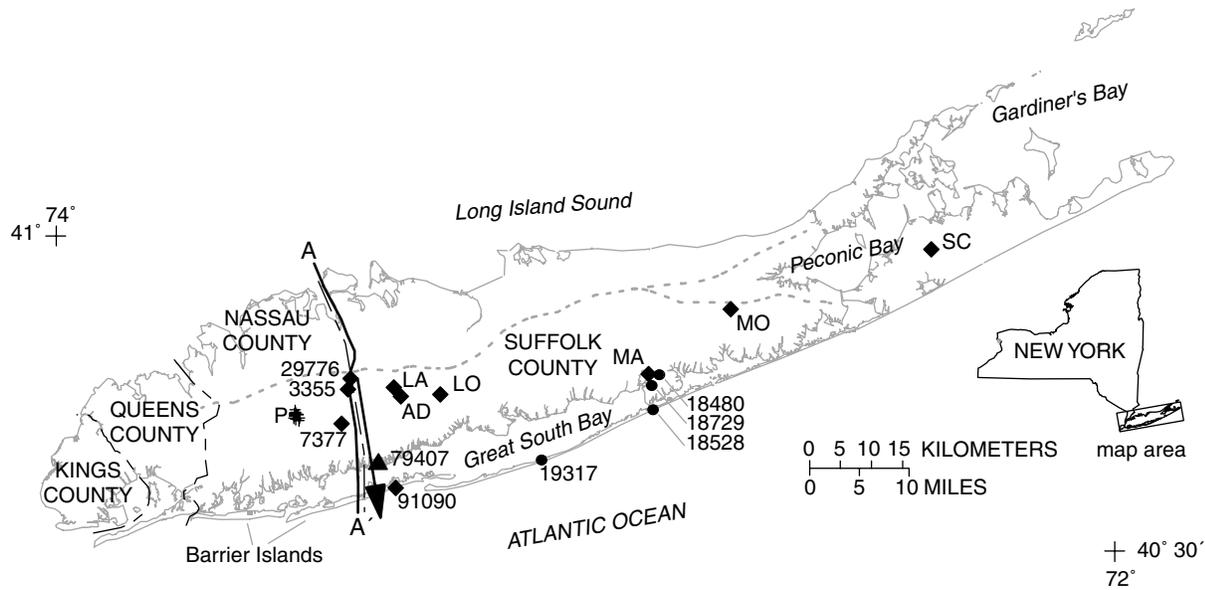
Purpose and Scope

This report describes the general abundance and distribution of iron-bearing minerals and other heavy minerals in the Pleistocene and upper Cretaceous deposits along the Nassau-Suffolk County border

about 1 km south of the ground-water divide, and compares these with data from sites farther along the flow path, and from other Long Island studies. It also describes the abundance and distribution of SOM in cores at borehole S79407T (on the barrier island), and the distribution and morphology of iron-sulfide minerals in sediments from SCWA borehole sites across Suffolk County (figs. 1 and 2).

Previous Heavy-Mineral Studies

Several hydrologic studies on Long Island have included mineralogical analyses. Suter and others (1949) listed the major- and trace-mineral constituents

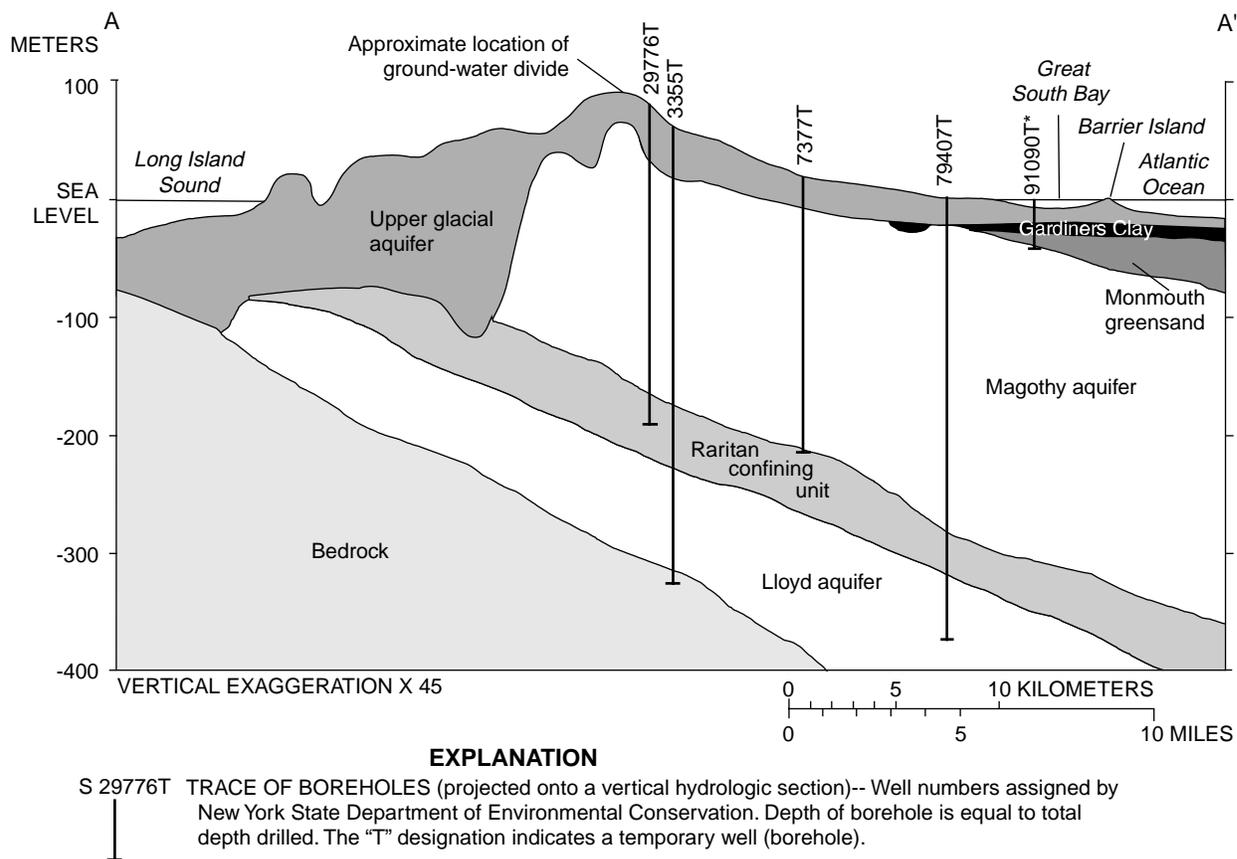


Modified base from New York State Department of Transportation, 1:24,000

EXPLANATION

- 29776 ◆ Borehole site studied (prefix S for Suffolk County and N for Nassau County is omitted)
- SCWA boreholes:
 - LA = Landscape Dr. AD = Adams Ave.
 - LO = Locust Dr. MA = Margin Dr.
 - MO = Moriches-Riverhead Rd. SC = Scuttlehole Rd.
- 19317 ● Borehole site studied by Perlmutter and Todd (1965)
- P ★ Borehole sites studied by Aronson and others (1983)
- 79407 ▲ Borehole site studied by Brenda Sirois and others (U.S. Geological Survey, written commun., 1986)
- Approximate location of ground-water divide
- A—A' Trace of vertical hydrogeologic section (depicted in fig. 2)
- Ground-water flow path

Figure 1. Locations of the borehole sites and line of section A-A' along Nassau-Suffolk County border, Long Island, N.Y. (Section A-A' is depicted in fig. 2.)



* borehole on the barrier island to the east and projected onto line of vertical section.

Figure 2. Hydrogeologic section A-A' along Nassau-Suffolk County border, N.Y., showing projections of nearby boreholes studied in this report. (Modified from Smolensky and others, 1989, sheet 1.) (Location is shown in fig. 1.)

in the Cretaceous and Pleistocene deposits. Faust (1963) found that the Pleistocene outwash sand in central Suffolk County contains greater quantities, and a greater variety, of heavy minerals, rock fragments, alkali feldspars, and hornblende than the upper Cretaceous deposits, which have a low detrital heavy-mineral content but contain lignite and pyrite. Perlmutter and Todd (1965) found that upper Cretaceous sand in southern Suffolk County contained the full suite of heavy minerals that is generally characteristic of the marine Cretaceous beds of Maryland, Delaware, and New Jersey; a "full suite" includes epidote, pyrite, ilmenite, garnet, zircon, sillimanite, staurolite, chloritoid, chlorite, muscovite, tourmaline, and glauconite (Groot and Glass, 1960). Brenda Sirois and others (U.S. Geological Survey, written commun., 1986) reported similar heavy-mineral occurrences in core samples from borehole S79407T on the barrier island (fig. 1).

Aronson and others (1983), in a geohydrologic study that included analysis of the textural

characteristics and heavy-mineral content in the upper glacial (Pleistocene) and Magothy (upper Cretaceous) aquifers, observed that (1) andalusite was present in Magothy deposits but absent from upper glacial deposits, whereas hornblende and clinozoisite were common in upper glacial deposits but absent from Magothy deposits; and (2) zircon, sillimanite, rutile, kyanite, garnet, and tremolite were present in considerably greater quantities in the upper glacial aquifer than in the Magothy aquifer. Foord and others (1970) used heavy-mineral, clay-mineral, and grain-size characteristics of cores from several deep boreholes in north-central Long Island to distinguish several units of upper Cretaceous and Pleistocene age. They found that the mostly nonmarine upper Cretaceous sediments were marked by a limited heavy-mineral suite and a lack of secondary minerals, such as glauconite. Liebling and Scherp (1975) reported a zone with abundant chlorite overlying the nonmarine Raritan Formation (Cretaceous). Brenda Sirois and others (written commun., 1986) found

similar abundances of chlorite in the cores at S79407T, as did Faust (1963) in upper Cretaceous samples from central Suffolk County.

Groot and Glass (1960), in a study of New Jersey coastal-plain sediments (Cretaceous and Cenozoic), observed two heavy-mineral suites—a full suite (as listed above) consisting of a variety of igneous and metamorphic minerals in marine sediments, and a limited suite characterized by highly stable minerals (tourmaline, zircon, rutile, and staurolite) in nonmarine sediments. Dryden and Dryden (1956) found that the limited suite in the nonmarine sediments did not contain garnet, epidote, chloritoid, or hornblende. Dryden and Dryden (1946), in a comparison of heavy-mineral-weathering rates in source rocks of Lower Cretaceous sediments in Maryland, found zircon, tourmaline, and sillimanite to be much more resistant than kyanite, hornblende, staurolite, and garnet. Owens and others (1960) showed through x-ray-diffraction analysis that “ilmenite” from the Miocene and Post-Miocene formations near Trenton, N.J., 55 km southwest of the study area, is a mixture of ilmenite and ferric and titanium oxides.

Brenda Sirois and others (written commun., 1986) examined several samples of cores for heavy minerals and SOM extending to a depth of 358 m in borehole S79407T (fig. 1) near the southern shore, and Perlmutter and Todd (1965) examined cores from several boreholes along the southern shore of Long Island. Brown and others (1999a) studied iron coatings, SOM content, and pyrite and marcasite in Magothy sediments on Long Island.

Study Methods

Cores for mineralogical analysis were obtained by borehole sampling. Laboratory procedures entailed (1) grain-size analysis, (2) heavy-mineral separation, and (3) mineralogical analysis.

Borehole Sampling

Split-spoon core samples used for the heavy-minerals analyses were collected during both previous studies and the present study. Boreholes were drilled by the reverse-rotary method, with the exception of S91090T, which was drilled by the cable-tool method. Previously collected core samples included six from Pleistocene (upper glacial) to upper Cretaceous (basal

Magothy) units from boreholes S29776T (Soren, 1971) and N3355T (N.M. Perlmutter and N.J. Lusczynski, U.S. Geological Survey, written commun., 1951) near the ground-water divide; one basal Magothy core from N7377T (midway along the flow path), and one cable-tool-bailer sample (Pleistocene) from S91090T (Scorca and others, 1995) on the barrier island (fig. 1). The altitudes, hydrogeologic units, and method of analysis for each sample are listed in table 1. The S79407T borehole was drilled by New York State Department of Environmental Conservation, and core samples were analyzed by Brenda Sirois and others (written commun., 1986). The split-spoon cores and drill-cuttings samples used for identification of organic-carbon content and iron-sulfide-mineral morphology were obtained from Magothy sediments from the six SCWA boreholes (fig. 1) by a reverse-rotary drill rig. During reverse-rotary drilling, large pieces of lignite or sand cemented with marcasite or pyrite were broken up by pulling the drill bit up several meters above the bottom of the hole and allowing the drill string to drop; fragments of the material were then removed by the circulated drilling fluids. Several cores from four of the boreholes were selected for analysis and were designated as AD1 through AD5 (Adams Avenue), LA1 through LA3 (Landscape Drive), LO1 through LO6 (Locust Drive), and MA1 through MA4 (Margin Drive) (table 1). A gamma log for these boreholes with a lithologic description and depth profile of organic carbon, total sulfur, and iron coatings in sediments, and of dissolved iron, sulfate, and dissolved organic carbon (DOC) concentrations in pore water, are given in Brown and others (1999a). Iron-sulfide mineral samples were collected from MO1 and MO2 at site MO (Moriches-Riverhead Rd.) and from an unknown altitude in the Magothy aquifer at site SC (Scuttlehole Rd.) (fig. 1).

Laboratory Analyses

Split-spoon core samples were analyzed for heavy minerals by the following procedures: A subsample of each core sample was disaggregated, and grain coatings were removed by sonic treatment in a 10-percent sodium bicarbonate solution according to the method of Cremeens and others (1987). Each sample was separated by mechanical sieves into five grain-size fractions, including material greater than 2 mm (granules and pebbles), 0.5 mm to 2 mm (coarse and very coarse sand), 0.125 to 0.5 mm (medium

sand), 0.00625 to 0.125 mm (very fine and fine sand), and less than 0.0625 mm (silt and clay). The silt and clay fractions were not analyzed in these cores, but results from a previous study of silt and clay mineralogy (Lonnie, 1982) are discussed further on. Heavy minerals (minerals with density > 2.75 g/cm³) were separated from each fraction with heavy liquids. Mineralogy of heavy-mineral fractions was determined through element analysis with Energy Dispersive Spectroscopy (EDS) on an electron microprobe analyzer; results are presented in Brown (1998).

Iron-sulfide minerals obtained from the six SCWA boreholes were identified by powder x-ray diffraction on a Scintag diffractometer. Scanning electron microscopy (SEM) was used to identify crystal morphology. X-ray maps of major elements in sediments were produced through wavelength-dispersive spectrometry (WDS) with a microprobe analyzer to delineate the element distribution and relations among iron-bearing minerals. Percentages of carbon forms and total sulfur in sediments were measured by combustion (Arbogast, 1996).

GEOLOGIC FRAMEWORK OF LONG ISLAND

Long Island consists of a sequence of upper Cretaceous, Pleistocene, and Holocene sediments that were deposited on a southeastward dipping Paleozoic and Precambrian bedrock surface (fig. 2). The deposits thicken toward the southeast and reach a maximum thickness of more than 610 m in southeastern Long Island (Smolensky and others, 1989).

Upper Cretaceous deposits include the Lloyd Sand Member (Lloyd aquifer) and the clay member of the Raritan Formation (Raritan confining unit), which are unconformably overlain by the Matawan Group and Magothy Formation (Magothy aquifer), undifferentiated (Smolensky and others, 1989). Along the southern shore of Long Island, the Matawan Group and Magothy Formation, undifferentiated, are unconformably overlain by the Monmouth Group (Monmouth greensand). Cretaceous sands on Long Island generally consist of chemically stable minerals or the highly altered equivalents of less stable minerals; in addition to angular quartz grains, they also contain tourmaline, rutile, zircon, kaolinite, kaolinized muscovite, weathered chert grains, and pyrite or marcasite associated with lignite (Suter and

others, 1949). The sediments that make up both the Raritan Formation and the Matawan Group and Magothy Formation, undifferentiated, were probably deposited in an environment that was dominated by streams and coalescing deltas (Buxton and others, 1981). The Matawan Group and Magothy Formation generally are considered to have been deposited in a nonmarine or transitional depositional environment; however, trace amounts of glauconite throughout Magothy aquifer sediments near the southern shore of southcentral Suffolk County indicate a transitional-to-marine depositional environment (Brown, 1998). The Monmouth Group, a marine deposit, typically consists of greenish-black glauconitic and lignitic clay, silt, and clayey to silty sand (Jensen and Soren, 1971). Upper Cretaceous marine clays of Long Island are primarily illite and montmorillonite with variable amounts of chlorite, glauconite, kaolinite, and mixed-layer clays, whereas upper Cretaceous nonmarine clays are primarily kaolinite with variable amounts of illite (Lonnie, 1982). Glauconite was found in Magothy sediments locally (Brown, 1998). Experimental work indicates that, at low temperatures and pressures, acid conditions favor kaolinite formation, whereas alkaline conditions promote the formation of smectites, or mica, if sufficient potassium is present (Deer and others, 1978). The upper surface of Cretaceous deposits in western Suffolk County ranges from more than 91 m above sea level near the approximate location of the groundwater divide (fig. 2), in an area known as the high Cretaceous terrace (Suter and others, 1949), to 30 m below sea level at the southern shore.

The Cretaceous deposits in the southern part of the island are unconformably overlain by the Gardiners Clay (an interglacial unit). North of this unit, they are unconformably overlain by deposits of Pleistocene age (upper glacial aquifer) (fig. 2). The Gardiners Clay is a dark-gray or greenish-gray silty clay or fine sand that may contain woody material, diatoms, foraminifera, and shell fragments (pelecypods) (Doriski and Wilde-Katz, 1983). The mineral assemblage of the Gardiners Clay commonly contains biotite, chlorite, glauconite, hornblende, muscovite, and quartz (Perlmutter and Todd, 1965) and a complete clay-mineral suite of illite, chlorite, mixed-layer clays, and minor kaolinite (Lonnie, 1982). Pleistocene marine clays, including the Gardiners, are illitic with variable amounts of chlorite,

Table 1. Altitude, hydrogeologic unit, and type of analysis performed on borehole samples from Nassau and Suffolk Counties, Long Island, N.Y.

[Altitudes are in meters above or below (-) sea level. Locations are shown in fig. 1]

Site identifier	Borehole site or sample	Altitude	Hydrogeologic unit	Type of analysis		
				Heavy minerals	Organic carbon	Iron-sulfide mineral morphology
N3355T	N1	32.8	Upper glacial aquifer	X		
	N1B	-82.0	Magothy aquifer	X		
S29776T	S1	14.3	Magothy aquifer	X		
	S2	-4.3	Magothy aquifer	X		
	S3	-53.3	Magothy aquifer	X		
	S4	-83.5	Magothy aquifer	X		
	S5	-163.1	Magothy aquifer	X		
N7377T	N2	-164.9	Magothy aquifer	X		
S79407T ¹	1	12.87	Upper glacial	X	X	
	2	-18.97	Gardiners clay	X	X	
	3	-25.1	Magothy aquifer	X	X	
	4	-25.2	Magothy aquifer		X	
	5	-25.37	Magothy aquifer	X	X	
	6	-34.5	Magothy aquifer	X	X	
	7	-53.4	Magothy aquifer	X	X	
	8	-70.49	Magothy aquifer	X	X	
	10	-91.8	Magothy aquifer	X	X	
	11	-176.6	Magothy aquifer	X	X	
	12	-217.7	Magothy aquifer	X	X	
	13	-251.6	Magothy aquifer	X	X	
	14	-294.3	Raritan confining unit	X	X	
	15	-304.3	Raritan confining unit	X	X	
	16	-316.5	Raritan confining unit	X	X	
	17	-338.5	Raritan confining unit	X	X	
	18	-344.6	Raritan confining unit	X	X	
	19	-350.7	Raritan confining unit	X	X	
	20	-356.2	Lloyd aquifer	X	X	
	S91090T	S6	-23.7	Gardiners clay	X	
Adams Ave. (S109640T) . . .	AD1	-118.7	Magothy aquifer		X	X
	AD2	-124.8	Magothy aquifer		X	
	AD3	-130.9	Magothy aquifer			
	AD4	-134.0	Magothy aquifer		X	X
	AD5	-137.0	Magothy aquifer		X	X
Landscape Dr. (S109750T) .	LA1	-146.9	Magothy aquifer		X	X
	LA2	-174.2	Magothy aquifer		X	
	LA3	-177.4	Magothy aquifer		X	
Locust Dr.	LO1	-145.0	Magothy aquifer		X	X
	LO2	-148.0	Magothy aquifer		X	
	LO3	-152.0	Magothy aquifer		X	
	LO4	-158.0	Magothy aquifer		X	X
Margin Dr. (S109249T) . . .	MA1	-142.4	Magothy aquifer		X	X
	MA2	-172.9	Magothy aquifer		X	
	MA3	-175.9	Magothy aquifer		X	X
	MA4	-179.0	Magothy aquifer		X	
Moriches-Riverhead Rd. . . . (S109074T)	MO1	-120	Magothy aquifer			X
	MO2	-197	Magothy aquifer			X

¹Collected and analyzed by Brenda Sirois and others, U.S. Geological Survey, written commun., 1986.

kaolinite, montmorillonite, and mixed-layer clays (Lonnie, 1982).

Upper Pleistocene deposits (upper glacial aquifer) are characterized mainly by clean, coarse sand but also contain sandy clay, clay, and fine sand; they may also contain the same minerals as the Cretaceous sediments but have a greater variety and abundance of heavy minerals such as amphibole, pyroxene, fresh muscovite, biotite, and chlorite, as well as rock fragments and unweathered feldspar (Suter and others, 1949). Pleistocene deposits in central Suffolk County typically contain rock fragments of chlorite schist (Faust, 1963). In general, upper glacial (Pleistocene) sands are coarser grained and contain a smaller silt and clay fraction than Magothy (Cretaceous) sands. Aronson and others (1983) found that Magothy aquifer sands in central Nassau County have a higher degree of sorting and a considerably smaller mean diameter than upper glacial sands. The upper glacial aquifer contains interstadial (nonglacial periods during Wisconsinan glaciation) clay units, including the “20-foot” clay (not shown in fig. 2), in the southern part of the study area (Doriski and Wilde-Katz, 1983), and the Smithtown clay (Krulikas and Koszalka, 1983), farther to the east (not shown in fig. 2). The “20-foot” clay has a mineral and fossil assemblage similar to that of the Gardiners Clay (Doriski and Wilde-Katz, 1983).

HEAVY MINERALS AND SEDIMENTARY ORGANIC MATTER

Core samples from boreholes at sites S29776T and N7377T, near the ground-water divide (fig. 1), were analyzed for heavy minerals; results were compared with data from previous studies to the south—at S79407T (Brenda Sirois and others, written commun., 1986) and several boreholes elsewhere in southern Suffolk County (Perlmutter and Todd, 1965). The sites of Brenda Sirois and others (written commun., 1986) and Perlmutter and Todd (1965) are collectively referred to herein as “southern-shore” sites unless discussed specifically. The following discussion includes data from other studies for comparison of spatial trends and of distribution of heavy minerals, SOM, iron, and sulfur among specific geologic units.

The most abundant mineral in upper glacial and Magothy sand is quartz, which typically constitutes at least 90 percent of the fine-to-coarse fraction; the heavy-mineral fraction generally constitutes less than

5 percent. Muscovite is more abundant in upper Cretaceous sand than in Pleistocene sand. The most commonly observed heavy minerals from boreholes near the ground-water divide (S29776T and N3355T, fig. 1) are listed in table 2A; the most abundant heavy minerals from boreholes along the southern shore (Brenda Sirois and others, written commun., 1986; Perlmutter and Todd, 1965) are listed in table 2B. SOM in Cretaceous deposits generally consists of lignite, which is found mostly as laminae or thin beds (fig. 3A) or as pieces of wood (figs. 3B, and 3C) in clay-and-silt beds, but also is disseminated in sands. Lignite diameter ranges from silt or clay size (≤ 0.062 mm) to > 200 mm.

Vertical Variations

The abundance of heavy minerals in sand fractions and SOM of core samples is somewhat dependent on the geologic unit and, therefore, the depth. The relative abundances of heavy minerals differ from unit to unit (table 2). These differences are probably a function of the extent of rock weathering (both mechanical and chemical) as well as the depositional environment. For example, Cretaceous sand has probably undergone more weathering and contains a smaller variety of heavy minerals than has Pleistocene sand (Faust, 1963). This difference may be smaller in poorly permeable units than in sand because the lower rates of ground-water flow would retard weathering. The depositional environment also can be important; for example, the Gardiners Clay and Monmouth greensand were deposited in a marine environment and contain abundant glauconite, a mineral typically absent in nonmarine sediments. Siderite was observed in an isolated core sample from the Raritan clay at borehole S79407T (Brenda Sirois and others, written commun., 1986), although most Long Island sediments contain no carbonate and contain ground water of low to moderate pH (5 to 7).

Several heavy-mineral differences between Pleistocene and Cretaceous sediments are evident at sites S29776T and N3355T, both at the Nassau-Suffolk County border (fig. 1). Relatively unstable minerals, including iron oxides, garnet, and rock fragments, are common in the Pleistocene sediments and less abundant or absent in Cretaceous sediments, whereas muscovite, which is generally considered to be stable, is more abundant in Cretaceous sediments than in Pleistocene sediments. Chloritoid and

Table 2. Most abundant heavy minerals (each less than 1 percent of heavy-mineral suite) in sand-size (0.0625-millimeter to 2-millimeter diameter) fractions of borehole cores from Suffolk and eastern Nassau Counties, Long Island, N.Y.

[Southern-shore data from Brenda Sirois and others (U.S. Geological Survey, written commun., 1986) and Perlmutter and Todd (1965). NA, not analyzed. Locations shown in fig. 1].

Series	A. Boreholes S29776T and N3355T near ground-water divide	B. Boreholes along southern shore
PLEISTOCENE	<p>Upper glacial aquifer Iron oxides, leucoxene, garnet (almandine), ilmenite, aluminosilicates, zircon</p>	<p>Upper glacial aquifer Hornblende, ilmenite, zircon, garnet, staurolite, kyanite, iron oxides, tourmaline, rock fragments</p> <p>Gardiners Clay Glauconite, hornblende, ilmenite, leucoxene, zircon, garnet, staurolite, epidote, tourmaline, pyrite/marcasite</p>
CRETACEOUS	<p>Magothy aquifer Muscovite, leucoxene, pyrite, ilmenite, rutile, staurolite, chloritoid, aluminosilicates, chlorite, zircon</p> <p>Raritan confining unit NA</p> <p>Lloyd aquifer NA</p>	<p>Monmouth greensand Ilmenite, leucoxene, muscovite, glauconite, zircon, pyrite, staurolite, garnet, tourmaline, sillimanite, epidote, chlorite</p> <p>Magothy aquifer Ilmenite/leucoxene, muscovite, hornblende, pyrite, marcasite, garnet, tourmaline, chlorite, staurolite, epidote, zircon, sillimanite</p> <p>Raritan confining unit Hornblende, staurolite, tourmaline, kyanite, muscovite, garnet, ilmenite/leucoxene, chlorite</p> <p>Lloyd aquifer Ilmenite/leucoxene, hornblende, staurolite, muscovite, tourmaline</p>

staurolite were also observed in Cretaceous sediments but not in Pleistocene sediments.

Heavy-mineral prevalence at the southern shore changes with depth. Pyrite or marcasite is generally present (and locally abundant) in Cretaceous sediments but is absent in Pleistocene sediments. Muscovite and chlorite are more abundant in Cretaceous sediments than in Pleistocene sediments, and, at borehole S79407T, tourmaline and staurolite are more abundant in Cretaceous sediments than in Pleistocene sediments. Biotite is rare or absent in the sediments of both ages at all sites. The presence of glauconite in the Monmouth greensand (Cretaceous) and the Gardiners Clay (Pleistocene) reflects the marine depositional environment of these units.

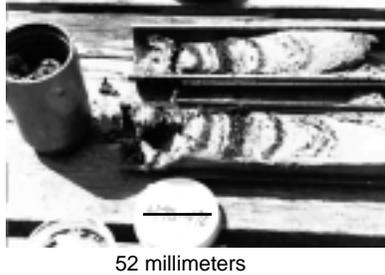
SOM content generally is low in Pleistocene deposits on Long Island but can be high in Cretaceous deposits (Brown and others, 1999a). SOM in Cretaceous deposits of Long Island generally is in the form of lignite; it affects the redox environment and the microbial communities as well as the distribution of iron oxide and iron-sulfide minerals (Brown and others, 1999a). The organic carbon content of cores from the borehole at site S79407 generally corresponds to the silt and clay content (fig. 4A) and the total sulfur content (fig. 4B). Plots of the log-

transformed data indicate that the silt and clay content shows a linear trend with the organic-carbon content ($r^2 = 0.31$; fig. 4C) and the total sulfur content shows a linear trend with the organic-carbon content ($r^2 = 0.72$; fig. 4D). This suggests that both SOM and sulfur in the form of iron-sulfide minerals are associated with silt and clay lenses. The vertical distribution of pyrite and marcasite at the four SCWA borehole sites is discussed further in the section "Distribution and Morphology of Pyrite and Marcasite."

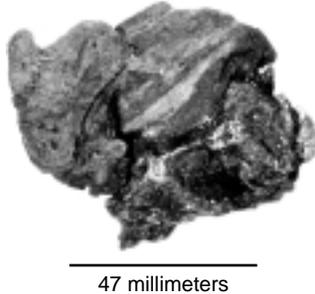
Lateral Variations

The lateral distribution of heavy minerals and SOM within lithologic units is not uniform throughout Long Island. For example, little or no hornblende was found in Magothy aquifer sediments near the ground-water divide (S29667T and N3355T). This trend was also observed by Aronson and others (1983) in central Nassau County, by Faust (1963) in central Suffolk County, and by Perlmutter and Todd (1965) at the southern shore, whereas relatively high percentages (up to 25 percent of the heavy-mineral suite) are reported throughout the Cretaceous sediments at S79407T by Brenda Sirois and others (written

A. Lignite laminae in Locust Dr. core sample



B. Lignite from Locust Dr. drill cuttings



C. Secondary electron image of lignite wood cells

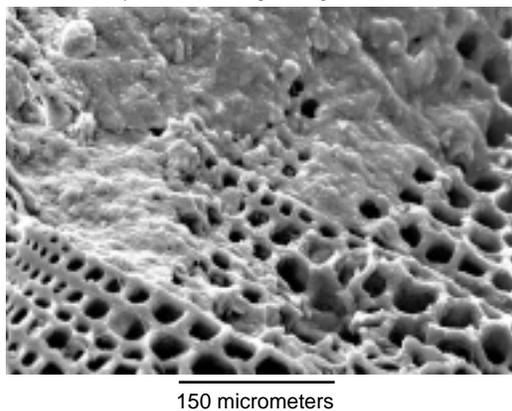


Figure 3. Photographs of lignite from Magothy aquifer, Suffolk County, N.Y.: A. Laminae or thin beds in split- spoon core sample. B. Lignite pieces from site LO. C. Secondary electron image of lignite wood cells from site AD. (Borehole- site locations are shown in fig. 1.)

commun., 1986). Glauconite typically is absent in the Matawan Group and Magothy Formation (Magothy aquifer), but is present in sediments from the site MA borehole near the southern shore (fig. 1) (Brown and others, 1999a). Pyrite or marcasite abundances in the Magothy aquifer also appear to vary laterally—borehole samples from near the ground- water divide contained much less iron-sulfide minerals

than those from near the southern shore, further along the ground- water flow path.

Abundances of iron-sulfide minerals and SOM in the Magothy also vary laterally. At short distances (4-7 km) from the divide, Magothy sand and gravel are generally yellow to brown, oxic, and contain little or no iron-sulfide minerals or lignite, whereas, the fine- grained Magothy sediments (those with a high percentage of silt and clay) are generally gray and anoxic (Brown and others, 1999a) and commonly contained iron-sulfide minerals and lignite. At distances of 10 to 20 km from the divide, sediments are more gray, and contain more iron disulfides and lignite than those close to the divide. Sediments with a high lignite content also had abundant iron-sulfide minerals. Site LO (fig. 1) had a high content of lignite and abundant pyrite and marcasite. The sediments at site LA contained little lignite, except at some depths, including sample LA1 (147 m below sea level) which was 8 percent organic carbon by weight. Samples LA2 and LA3 contained no SOM (Brown and others, 1999a).

The distributions of other heavy minerals at boreholes near the divide also differs significantly from those at the southern shore along section A-A'. Garnet and tourmaline are extremely sparse in Magothy sediments at sites S29776T and N3355T, near the divide, but are reported throughout southern- shore deposits (Brenda Sirois and others, written commun., 1986; Perlmutter and Todd, 1965), whereas rutile is abundant throughout upper glacial and Magothy sediments near the divide but is rare or absent in southern-shore deposits. Aluminosilicates (used herein to refer to kyanite, sillimanite, and andalusite) were abundant throughout Magothy and upper glacial cores from near the divide (S29776T and N3355T) but could not be distinguished from one another by this author using EDS. Kyanite and sillimanite were reported in high to moderate abundance in cores from the southern shore, but andalusite was not. Sheet silicates that are locally abundant in the Magothy include chlorite, chloritoid, and amesite; chloritoid and amesite were particularly abundant in cores from N7377T (fig. 1). Glauconite, another sheet silicate, is abundant in the Monmouth greensand and the Gardiners Clay (marine deposits beneath the southern shore), and in the Magothy aquifer near the southern shore (site MA) but does not extend to the northern part of section A-A'. An indurated, iron-cemented sand was found in a sample

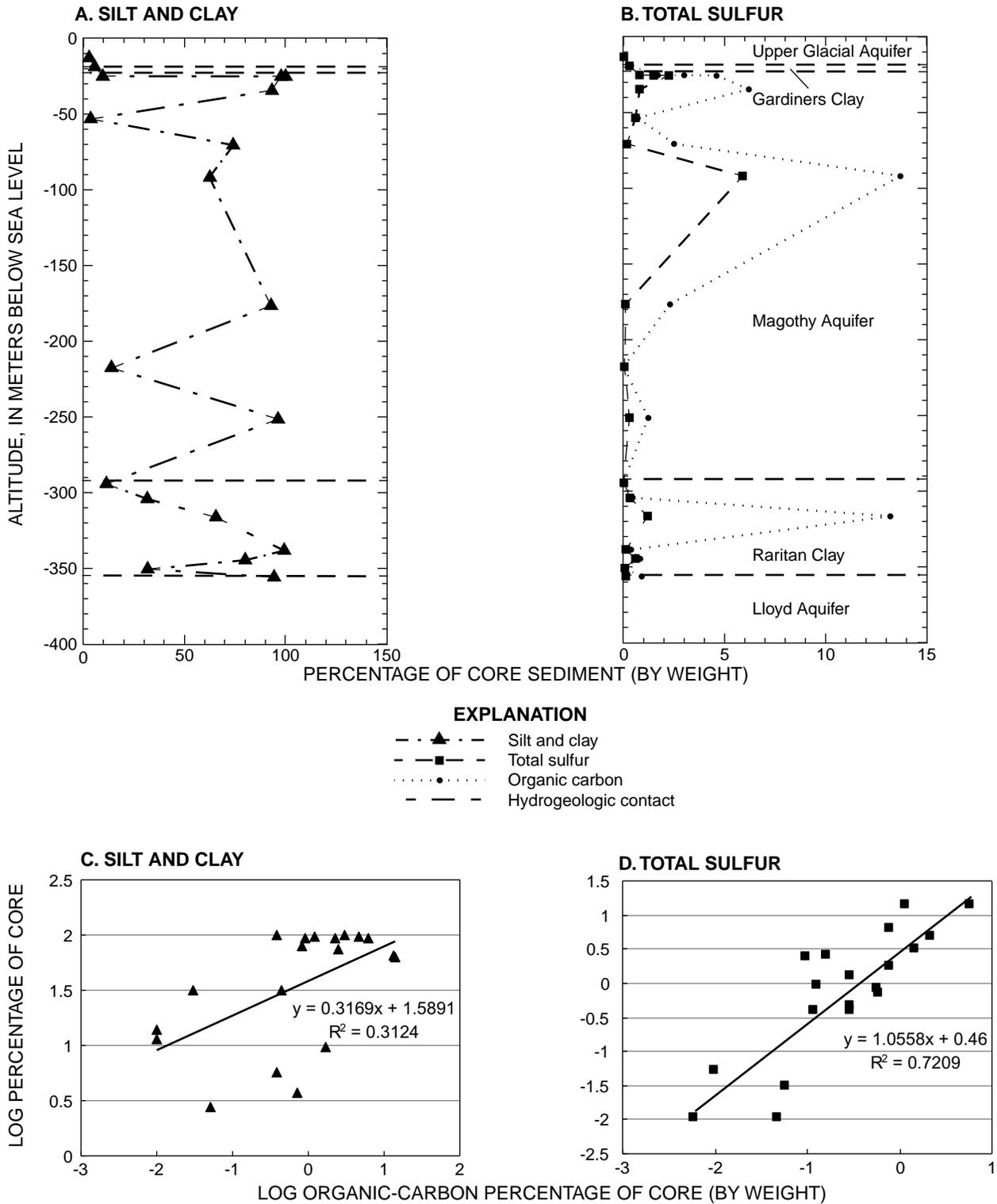


Figure 4. Abundance of (A) silt and clay, and (B) total sulfur and organic carbon, in core samples relative to altitude below sea level; and log percent (C) silt and clay, and (D) total sulfur, as a function of log organic carbon percentage of core samples from borehole S79407T, Suffolk County, N.Y. (Data from Brenda Sirois and others, U.S. Geological Survey, written commun., 1986; borehole location is shown in fig. 1)

from 21.9 to 23.7 m below sea level at S91090T on the southern barrier island. Cements in part of this sample also contained calcium and manganese, as indicated by microprobe analysis with EDS, and may be ankerite; the calcium may have originated through the upward flow of ground water through the Gardiners Clay, which contains calcite.

The most abundant heavy mineral near the divide is leucoxene, an altered iron titanium oxide that was found throughout the core samples from borehole S29776T and in samples from N3355T and N7377T. The leucoxene at these boreholes appears similar to the "ilmenite" of the Miocene and post-Miocene formations in southern New Jersey, which is reported as a mixture of ilmenite and ferric and titanium oxides (Markewicz and others, 1958). SEM analysis of leucoxene grains from sample N2 at site N7377T (164.3 to 144.9 m below sea level) and from N1B at site N3355T (81.7 to 82 m below sea level) along section A-A' have extensive etching that indicates weathering. Leucoxene from N1 at N3355T, observed with reflected light and EDS, shows the blocky structure and slightly pinkish color of ilmenite, which was mostly altered to hematite (Donald Lindsley, State University of New York at Stony Brook, oral commun., 1995). Abundant leucoxene and ilmenite also were found along the southern shore by Perlmutter and Todd (1965). Brenda Sirois and others (written commun., 1986) did not distinguish between the opaque minerals at site S29776T, which include leucoxene and ilmenite. Zircon was found in moderate to high abundance throughout the study section, which includes both Cretaceous and Pleistocene deposits.

Grain size

Heavy minerals near the ground-water divide typically are concentrated in the very-fine sand and fine sand fractions of the Cretaceous and Pleistocene sediments. This distribution has been attributed to geological, mineralogical, and sedimentological factors (Rittenhouse, 1943). In central Suffolk County, the heavy mineral abundance in Pleistocene sediment has been reported to be greater in sand fractions less than 0.125 mm (fine sand to silt and clay) than in the medium and coarse sand fractions (Faust, 1963), whereas at site S79407T, near the divide, the heavy-mineral abundance of silt and clay fractions does not appear to differ significantly from that in sand fractions. The presence of Fe, Ti, and S peaks in x-ray

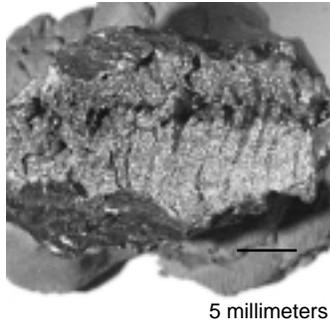
fluorescence analyses in south-shore sediments analyzed by Brenda Sirois and others (written commun., 1986), and the sulfur percentages (fig. 4), suggest the presence of both (1) iron oxides or hydroxides, or (2) TiO_2 or FeTiO_2 , such as rutile, ilmenite, or leucoxene, and (3) pyrite or marcasite, in silt and clay fractions and in sand fractions.

PYRITE AND MARCASITE IN THE MAGOTHY AQUIFER

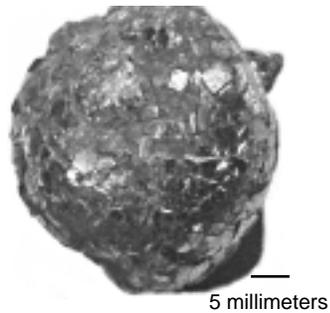
The distribution and morphology of the iron disulfides (pyrite and marcasite) in the Magothy aquifer are discussed here because they are particularly important to the solubility of iron in ground water (Brown and others, 1999a). The precipitation of iron-sulfide minerals in sulfate-reducing TEAP zones results in the removal of sulfate and iron from solution, given a sufficient supply of an electron donor (lignite) for sulfate-reducing organisms. In oxic zones, however, iron-sulfide minerals are oxidized, which results in the release of iron back into solution (Brown and others, 1999a). Iron-sulfide minerals from the SCWA boreholes (fig. 1) were analyzed for morphology and distribution; SOM-content data from these boreholes were also analyzed and compared to previously-collected data (Brenda Sirois and others, written commun., 1986; Brown and others, 1999a).

Pyrite, which is the thermodynamically stable iron disulfide in most anoxic sedimentary environments, was generally found as crystals directly on (fig. 3B), within (fig. 5A), or surrounding (fig. 5B) the wood structure of lignite. Marcasite, which is a dimorph of pyrite, was found in interbedded sand as interstitial cement (fig. 5C), commonly to the point of virtually eliminating porosity. Pyrite initially nucleates on the Fe(II) monosulfide surface but subsequently nucleates on older pyrite (Schoonen and Barnes, 1991). Fe(II) monosulfides were not observed, however, in Magothy sediments. Much of the pyrite in these samples may have formed thousands of years ago, perhaps shortly after deposition of the sediments, and has been protected against oxidation by its association with lignite and fine-grained sediments. Marcasite could form only under the low-pH conditions (Murowchick and Barnes, 1986) provided by pyrite oxidation, and, therefore, could form only after the earliest pyrite had already formed.

A. Pyrite crystals within lignite at Locust Dr.



B. Pyrite crystals around lignite at Scuttlehole Rd.



C. Interstitial marcasite and quartz at Adams Ave.

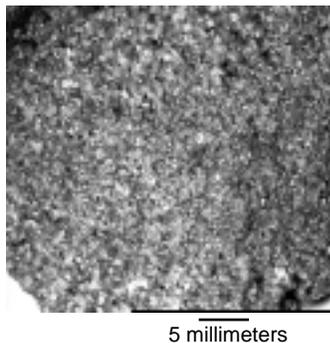


Figure Figure 5. Photographs of pyrite and marcasite from the Magothy aquifer in Suffolk County, N.Y.: A. Pyrite crystals within lignite from site LO. B. Pyrite crystals in a spheroid aggregate from site SC. C. Interstitial marcasite in quartz sand from site AD. (Borehole-site locations are shown in fig. 1.)

Ground water near the divide generally is oxic, but localized lignitic, sulfate-reducing zones favor the preservation and(or) formation of pyrite and marcasite. Magothy sediments at borehole-site AD (near the ground-water divide, fig. 1) generally contained a greater abundance of iron-sulfide minerals than did those at the nearby borehole at site LA; probably because site AD contains greater amounts of

SOM, which result in larger sulfate-reducing zones (Brown and others, 1999a). Etched pyrite and low-pH pore waters found at the perimeter of these zones indicate iron-sulfide-mineral oxidation (Brown and others, 1999a).

Mineralogic and Lithologic Description of Selected Sediments

The following section presents a mineralogic and lithologic description of selected sediments from drill cuttings or core samples from Suffolk County Water Authority boreholes, with respect to pyrite and marcasite.

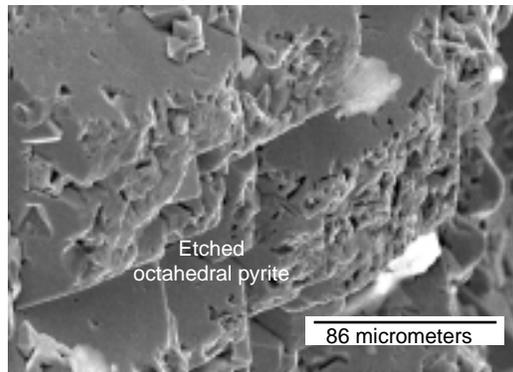
Landscape Drive Cores (Site LA)

Magothy sediments from core sample LA1 (from site LA) were a grayish-black, sandy clay with laminae of lignitic silt and a 2- x 3-cm piece of pyrite partly surrounded by dark-gray lignitic clay. Secondary electron images (SEI) of crystals on part of the pyrite sample show etching (figs. 6A and B), which indicates pyrite oxidation. Etching of the octahedral pyrite crystals from this sample (fig. 6B) appears to be random, but octahedral crystals in other parts of the same sample (fig. 6A) show localized etching on parts of the crystal. This differential etching may result from (1) compositional and structural differences that would cause segregated etching, or (2) two generations of crystal growth, that is, an initial pyrite growth followed by pyrite oxidation, perhaps brought on by a period of oxidizing conditions, then further growth of pyrite over the etched crystals. Oxidation of pyrite generally occurs on reactive sites of high excess surface energy, such as grain edges and corners, defects, solid- and fluid-inclusion pits, cleavages, and fractures (McKibben and Barnes, 1986).

Adams Avenue Cores (Site AD)

Pyrite was found on lignite and as interstitial cement in Magothy sediments from site AD at depths of 110 m, 117 m, and 121 m below sea level, and marcasite was found as interstitial cement at depths of 110 m, 117 m, and 118 m below sea level. Pyrite crystals from 117.2 m below sea level, which were taken 1.5 m above core sample AD1, were etched (fig. 7A) and, therefore, indicate pyrite oxidation. A TEAP assay of AD1 sediment, which is a brownish-gray sand with pockets of light olive-gray, lignitic

A. Random etching



B. Localized etching

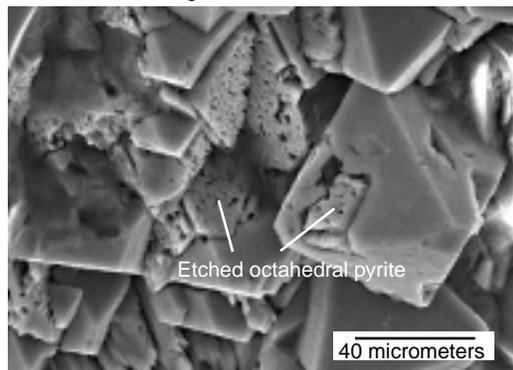


Figure 6. Scanning-electron microscope images showing etched octahedral pyrite crystals from site LA, Suffolk County, N.Y. (sample LA1; altitude 146.9 meters below sea level): A. Random etchings. B. Localized etching.

sandy clay, showed that no reducing bacteria were present (Brown and others, 1999a). The etched pattern appears to be random (fig. 7A), similar to that at site LA (fig. 6A), and may reflect the lignite surface over which the pyrite formed. The low pH of pore water downgradient from zones of pyrite oxidation (Brown and others, 1999a) is conducive to the formation of marcasite. Etching was not observed on other iron-sulfide minerals from this borehole, including marcasite- and pyrite-cemented sand (fig. 5C) at 110 m below sea level; this indicates the presence of localized redox microenvironments. The marcasite cement at 118 m below sea level (fig. 7B) had platy crystals (fig. 7C) that show parallel growth steps (fig. 7D). Marcasite- and pyrite-cemented lignite and sand at 117 m below sea level contained marcasite crystals that showed cockscomb growth (fig. 7E). Part of this sample had a red coating that could be a

ferric hydroxide mineral, which would indicate locally oxic conditions.

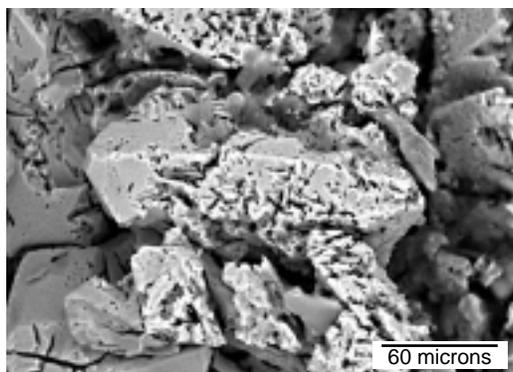
Locust Drive Cores (Site LO)

Magothy cores from site LO contained abundant lignite and pyrite associated with clay lenses. At many depths, much of the sand between clay lenses was cemented with marcasite. The repetitive occurrence of pyrite in the clay lenses, and of marcasite in the sand between the clay lenses, suggests that pyrite was oxidized from the clays and reprecipitated as marcasite in areas of low pH (Brown and others, 1999a). Pyrite in clays deficient in oxygen, can be oxidized by Fe(III), which is soluble in pore waters of low pH (<3) and reacts with pyrite faster than oxygen (McKibben and Barnes, 1986; Moses and others, 1987; Brown, 1998). SEI images of pyrite and marcasite from the LO site show cubo-octahedral pyrite crystals (fig. 8A) that have grown inside the remnant wood cells, and octahedral pyrite crystals (figs. 8A and 8B) that have grown over the lignite and cubo-octahedral pyrite. The presence of iron-sulfide minerals within isolated or “closed” microenvironments devoid of iron, such as within wood cells (fig. 8A), suggests that significant amounts of iron may be present as sulfide complexes in solution (Rickard and others, 1995). Platy marcasite crystals similar to those found at site AD (figs. 7B, C, D) were found in sediments near the pyrite at 163.5 m below sea level.

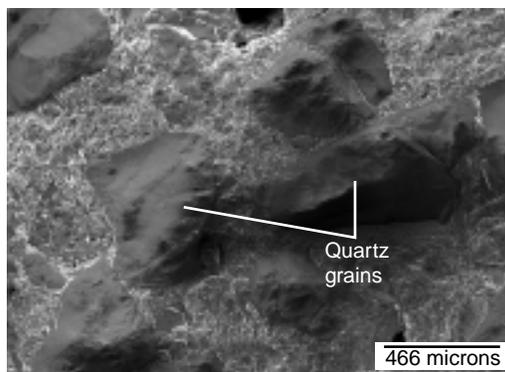
Margin Drive Cores (Site MA)

Iron-sulfide minerals at site MA near the southern shore in Suffolk County (fig. 1) were present in clayey lenses as pyrite grains and pyritized lignite, and in sandy beds as interstitial pyrite and marcasite cement, as in the cores from site LO midway between the ground-water divide and the shore. Most of the cement consisted of pyrite, but x-ray diffraction analysis of iron-sulfide-cemented lignite from sediments from 117 m below sea level indicated mostly marcasite with some pyrite. The presence of marcasite at this depth suggests the marcasite formed in a low-pH environment that probably resulted from pyrite oxidation. Given the oxic conditions that are generally found at that great a distance from the divide, oxidation of pyrite may have occurred through reduction of Fe(III) oxyhydroxides, or alternatively, a period of anoxic conditions may have resulted from a

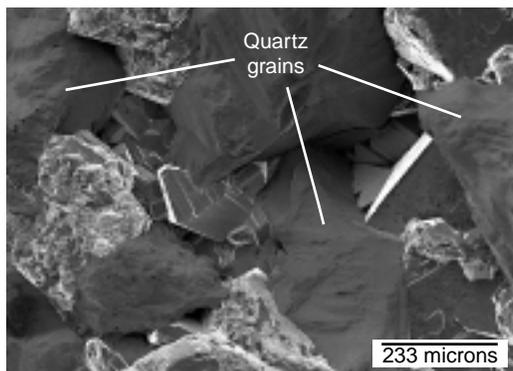
A. Etched octahedral pyrite



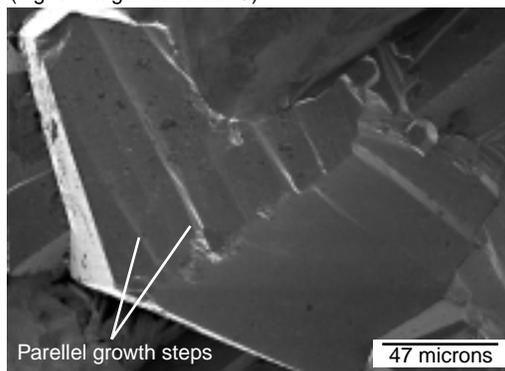
B. Interstitial marcasite cement



C. Platey marcasite crystals



D. Parallel growth steps of platey marcasite crystals (higher magnification of C)



E. Cockscomb marcasite

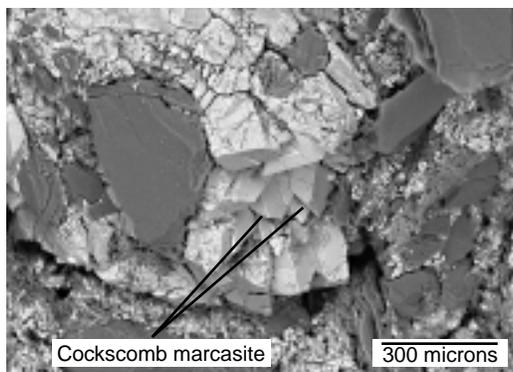


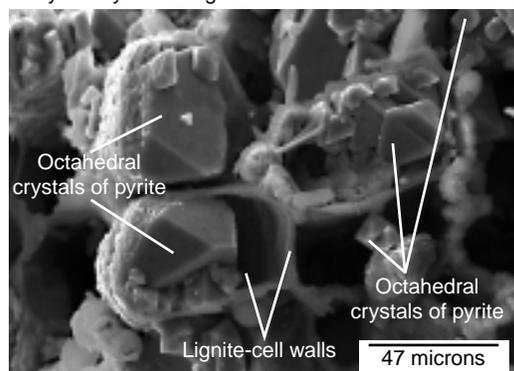
Figure 7. Scanning-electron microscope images of iron-sulfide minerals from site AD, Suffolk County, N.Y.: A. Etched octahedral pyrite crystals from 117.2 m below sea level. B. Interstitial marcasite cement. C. Platey marcasite crystals in marcasite cement. D. Parallel growth steps of platey marcasite. E. Cockscomb marcasite from 117 m below sea level. (Borehole-site location is shown in fig. 1.)

rise in sea level during the Pleistocene (Brown, 1998). SEI of the sample shows cockscomb-growth marcasite crystals overgrown with smaller crystals of octahedral pyrite (fig. 9A); this suggests two generations of growth, wherein the change from marcasite to pyrite growth indicates an increase in pH of pore water. Other parts of the same sample contained mostly pyrite, and crystals were octahedral, cubo-octahedral (fig. 9B), and in framboidal aggregates (fig. 9C). The presence of framboidal pyrite among octahedral pyrite

crystals suggests that they were formed from a local, reactive iron source (Raiswell, 1982). Cubo-octahedral pyrite crystals on another part of the same sample are poorly formed (fig. 9B), and pits on the surface probably represent an incomplete growth layer.

Pyrite growth on lignite surfaces generally is octahedral; backscatter electron imaging (BEI) of a sample from 176 m below sea level at site MA (fig. 1) shows octahedral pyrite growth directly on a “twig” of lignite (fig. 9D). SEI of a large (50 mm) sample of

A. Pyrite crystals in lignite



B. Octahedral pyrite

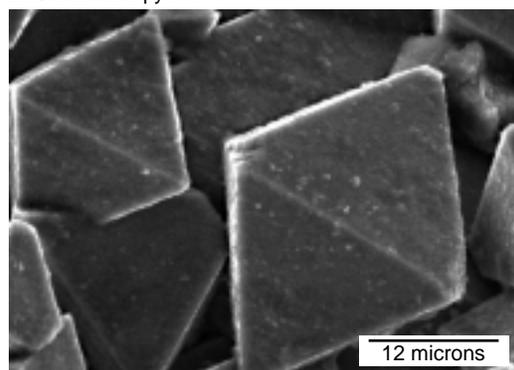


Figure 8. Scanning-electron microscope images of samples from site LO, Suffolk County, N.Y.: A. Pyrite crystals and lignite wood-cell structures. B. Octahedral pyrite crystals. (Borehole-site location is shown in fig. 1.)

cubo-octahedral pyrite from 167 m below sea level shows unusual secondary nucleation and growth features (fig. 9E) that are found in galena. Iron-sulfide cements at other depths (136, 141, 145, 154, and 176 m below sea level) consisted of pyrite and completely filled the pore spaces of sand at several depths. Leucoxene, chlorite, and glauconite commonly were found in association with iron-sulfide cement and may be sources of iron for the formation of iron-sulfide minerals. The extractable-Fe(II) content of sediment from MA1, from 142 m below sea level, was high (80 $\mu\text{mol/g}$) and may be derived from iron-bearing clay minerals that were found in this core sample, such as glauconite (fig. 9F) or chlorite (Brown, 1998). Sample MA3, from 176 m below sea level, had a 5-cm-thick piece of pyrite-cemented sand near its top. Iron-sulfide samples from depths of 117 m and 175.6 m below sea level (core MA3) consist of a matrix of sand-sized grains that include quartz, lignite, and leucoxene (iron

titanium oxide) cemented with pyrite (fig. 12). The locally abundant leucoxene may be an iron source for the formation of pyrite.

Moriches-Riverhead Road Cores (Site MO) and Scuttlehole Road Cores (Site SC)

Iron-sulfide mineral cement in Magothy cores from site MO, near the ground-water divide in eastern Suffolk County (fig. 1), ranged from mostly pyrite with a small amount of marcasite at 120 m below sea level, to soft, poorly crystalline marcasite cement with stalactite-shaped crystals (fig. 10) at 197 m below sea level. Marcasite from a cemented-sand sample from site AD had a similar, soft consistency.

Cubic pyrite “balls” (fig. 5B) were abundant in Magothy sediments from site SC, on the South Fork of eastern Suffolk County (fig. 1). Interlocking cubic {100} crystals were observed on the outer surface (fig. 11A, 11B). A section through the center of the pyrite ball shows elongate, wedge-shaped crystals radiating from the center (fig. 11C, 11D). Small lenticular pieces of lignite near the center of the ball (fig. 11C) appear to represent the substrate around which the pyrite nucleated.

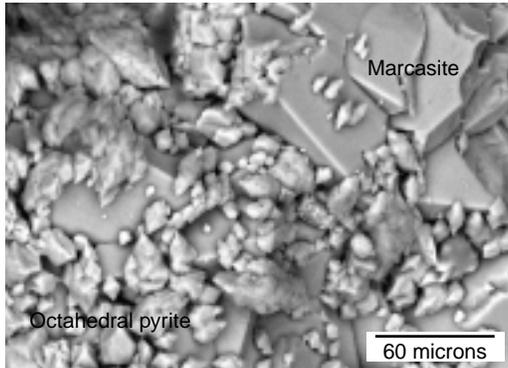
Mineral Reactivity

Mineral reactivity is an important factor in ground-water chemistry. Iron-bearing minerals such as ferrihydrite (poorly ordered ferric oxyhydroxide), goethite, hematite, glauconite, and chlorite are more reactive than minerals such as ilmenite, garnet, augite, and amphibole (Canfield and others, 1992). Chlorite contains abundant iron and may be an important source of iron in the Magothy aquifer. Glauconite probably weathers to goethite (Wolff, 1967) as indicated by the high concentrations of cations and silica in ambient ground water (Brown, 1998). Amorphous ferric oxyhydroxide or poorly ordered ferric oxyhydroxide (ferrihydrite) are considered to be reactive or microbially reducible (Chukhrov and others, 1973; Lovley and Phillips, 1986a), whereas other iron forms, including hematite and magnetite, are not readily reducible (Lovley and Phillips, 1986b) but could be biomineralized by dissimilatory iron-reducing bacteria (Caccavo, 1999), or slowly reduced by Fe(III)-reducing organisms in systems in which decomposition of organic matter is dominated by sulfate reduction or methane production (Lovley, 1987). Leucoxene grains were locally abundant in iron sulfide-cemented sand from 117.4 m below sea level at

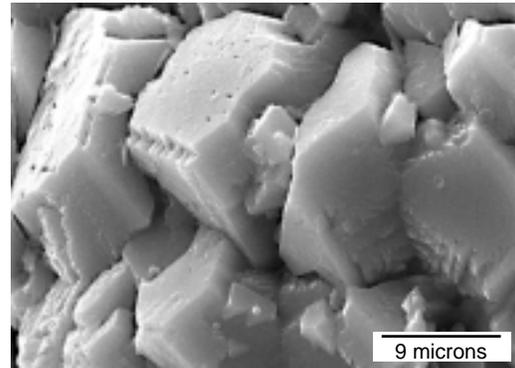
southern-shore site MA and probably represent an iron source for the formation of iron-sulfide minerals. Wavelength-dispersive-spectrometry maps of the distribution of aluminum, titanium, iron, and sulfur show iron-bearing minerals among quartz and lignite grains that are surrounded by pyrite cement (fig. 12).

Leucoxene and chlorite are among the iron-bearing minerals identified by EDS and may represent a reactive source of iron for the formation of the pyrite cement. Much of the leucoxene is associated with TiO_2 (probably rutile). The low concentrations of sulfide in Magothy ground water, despite the high

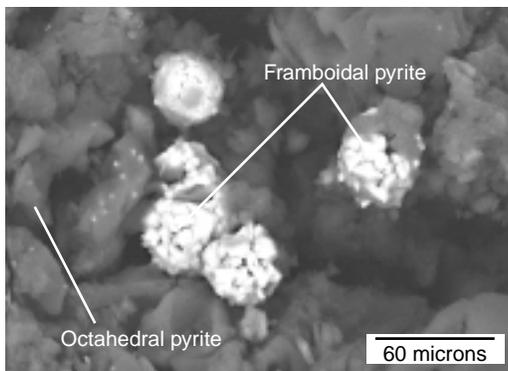
A. Marcasite and pyrite



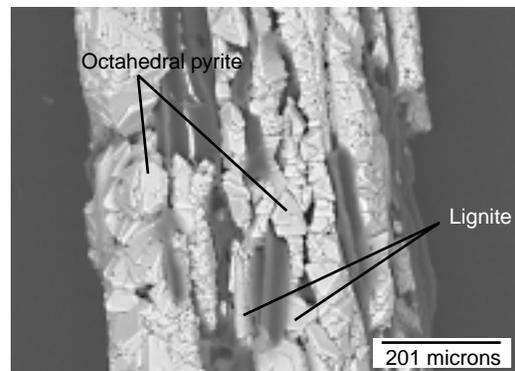
B. Cubo-octahedral pyrite



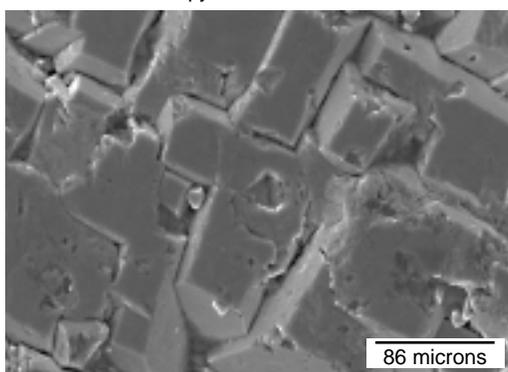
C. Framboidal and octahedral pyrite



D. Octahedral pyrite on lignite



E. Cubo-octahedral pyrite



F. Glauconite

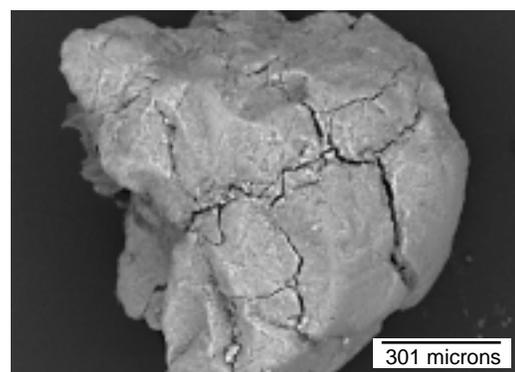


Figure 9. Scanning-electron microscope images of samples from site MA near the southern shore of Suffolk County, N.Y.: A. Cockscomb-growth marcasite crystals overgrown with smaller crystals of octahedral pyrite. B. Cubo-octahedral pyrite crystals. C. Framboidal pyrite. D. Octahedral pyrite on lignite. E. Cubo-octahedral pyrite. F. Glauconite. (Site location is shown in fig. 1.)

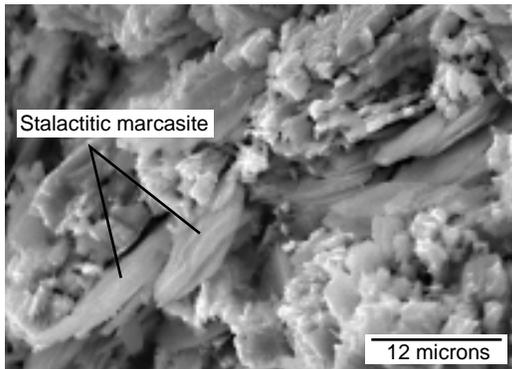


Figure 10. Scanning-electron microscope image showing poorly crystalline marcasite cement with stalactite-shaped crystals from site MO, Suffolk County, N.Y. (Location is shown in fig. 1.)

concentrations of sulfate and the predominance of sulfate-reducing TEAPs, suggest that sulfides generally react rapidly enough with iron to form iron-sulfide minerals.

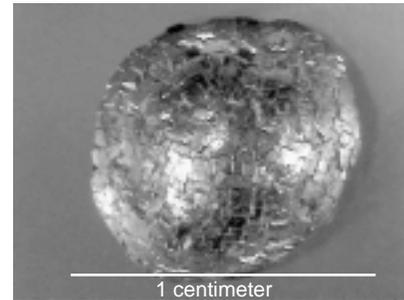
The high percentage of iron-sulfide cement (about 50 percent) in the sample from site MA (fig. 12) suggests that the initial porosity of the sediment (immediately after deposition) was high relative to the current average porosity of Magothy aquifer sediments (25 to 30 percent; McClymonds and Franke, 1972). Therefore, this pyrite may have formed during early diagenesis, before compaction by overlying sediments.

Local variations in the concentrations of Fe(III) oxyhydroxides at site MA suggest that localized abundance of microbially available Fe(III) promote the activity of iron-reducing bacteria (IRB). Leucoxene also may provide a local source of Fe(III) for IRB. Fe(III) in core sediments from MA4 was reduced in the laboratory after the sediments were inoculated with an iron-reducing organism (strain MD-612) and amended with acetate; this indicates that Fe(III) coatings in these Magothy sediments are available to the indigenous microbial population, and that the activity of the IRB is limited by the amount of electron donor (organic carbon) available, and not by the availability of Fe(III) (Brown and others, 1999a).

SUMMARY AND CONCLUSIONS

The types of iron-bearing minerals and their distribution within an aquifer system are important factors to consider for the study of iron geochemistry and the causes of biofouling and encrustation of wells.

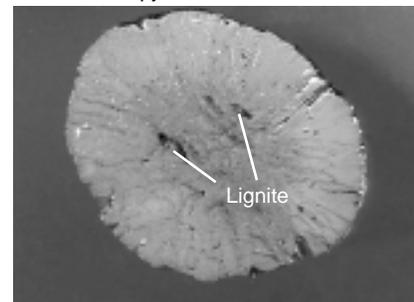
A. Pyrite ball



B. Magnified image of cubic crystals



C. Section of pyrite ball



D. Magnified image of pyrite

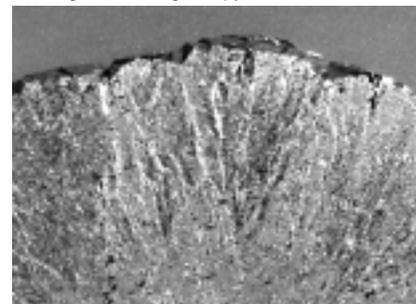
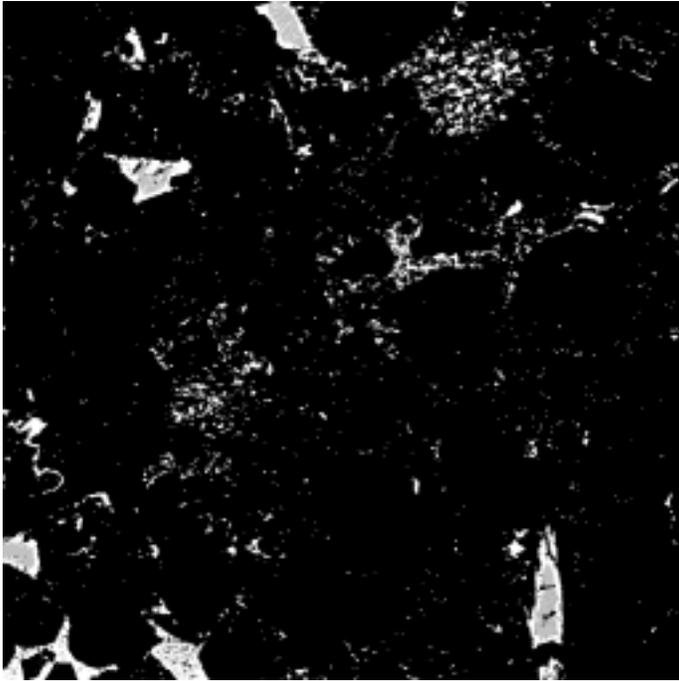


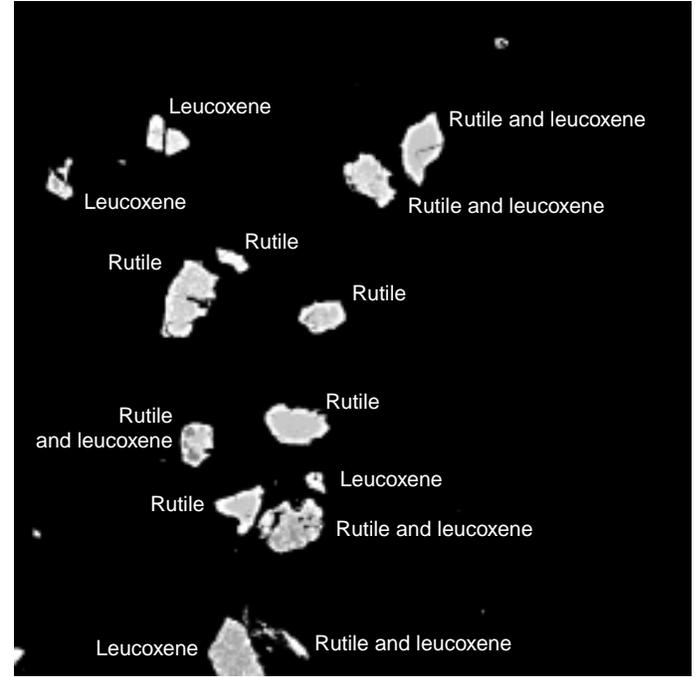
Figure 11. Cubic pyrite from site SC, Suffolk County, N.Y.: A. "Ball," about 1 centimeter in diameter. B. Interlocking cubic {100} crystals in surface of "ball." C. Section of "ball" showing wedge-shaped crystal radiating from the center. Arrows near center indicate lenticular lignite pieces. D. Magnified image showing the internal radial texture of thin section depicted in fig. C. (Borehole-site location is shown in fig. 1.)

A. Aluminum

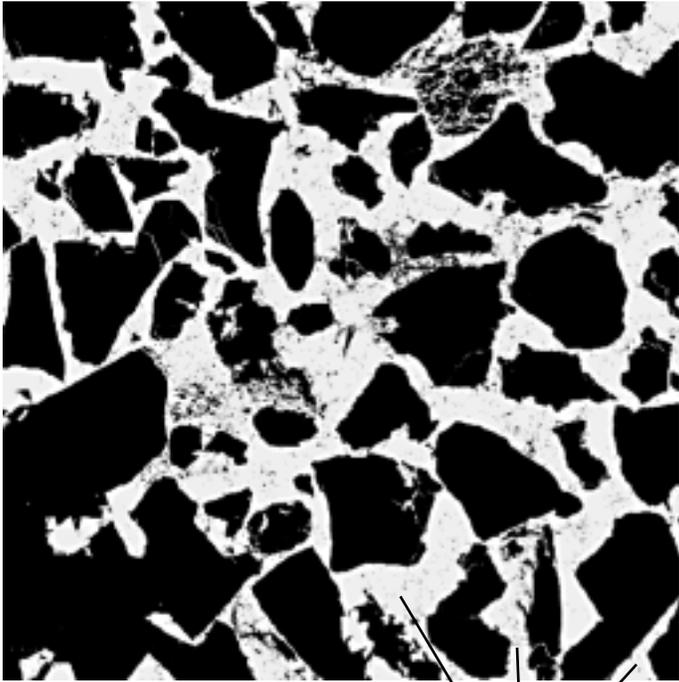


0.5 millimeters

B. Titanium



C. Sulfur



Pyrite cement

D. Iron

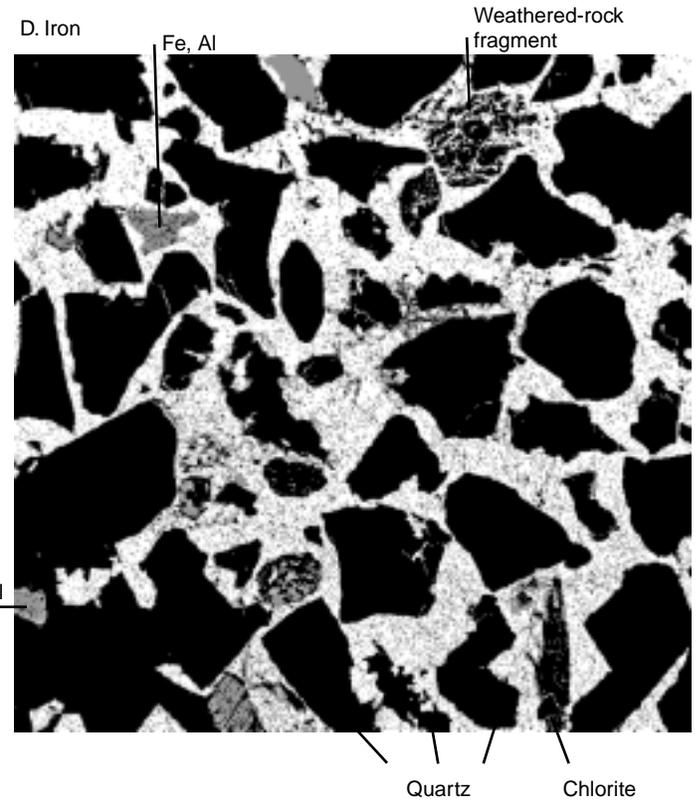


Figure 12. Wavelength-dispersive spectrometry maps showing the distribution of selected elements associated with iron-bearing minerals and rutile among quartz grains surrounded by pyrite cement from site MA site near southern shore of Suffolk County, N.Y. (Location is shown in fig. 1).

The lateral distribution of iron-bearing and other heavy minerals within lithologic units is not uniform throughout Long Island, or even along the study section on the Nassau-Suffolk County border. Mineralogy and mineral abundance in Pleistocene units differs from those in Cretaceous units, and some of the trends vary with depth as well as from north to south. Upper Pleistocene sediments along the section contain more unstable rock fragments and minerals, such as garnet and iron oxides, than the Cretaceous deposits, which contain abundant muscovite, staurolite, pyrite or marcasite, and chloritoid. Borehole samples from oxic zones (near the ground-water divide) contain less pyrite or marcasite than those from boreholes in anoxic zones (near the southern shore, farther along the ground-water flow path) because iron-sulfide minerals are less likely to be preserved or formed under oxic conditions. Glauconite is abundant in the Monmouth greensand, the Gardiners Clay, and in parts of the Magothy aquifer that are marine or transitional-to-marine deposits beneath the southern shore but is absent in the northern part of the study section. Heavy minerals are typically concentrated in the very-fine sand and fine-sand fractions of Pleistocene and Cretaceous sediments.

Leucoxene, iron oxyhydroxides, glauconite, chlorite, pyrite, and marcasite were the most abundant and potentially reactive of the iron-bearing minerals detected, with the exception of Fe(III) oxyhydroxide grain coatings. Ferric oxyhydroxide coatings on sediment grains are an important sink as well, but other more highly crystalline Fe(III)-bearing minerals may also be biomineralized in anoxic environments by Fe(III)-reducing organisms. Leucoxene was observed in relatively large abundance throughout Long Island sediments and may represent an important iron source. Iron sulfides are a major iron sink for dissolved iron in the Magothy aquifer and can be a source of dissolved iron through oxidative dissolution.

Some microbial and geochemical environments can be inferred from the presence and morphology of pyrite or marcasite. Pyrite was generally found in association with lignite or as interstitial cement. Marcasite was found as interstitial cement and presumably is associated with oxidation of upgradient iron-sulfide minerals. Pyrite crystals were octahedral, cubic, cubo-octahedral, and framboidal, and some specimens showed more than one generation of crystal growth. Marcasite cement, which in most samples consisted of platy crystals, probably forms only at the

low pH range of nonmarine conditions. Iron-bearing minerals in the aquifer system, therefore, can be both a source and a sink for dissolved iron in ground water and their distribution along the flow path can affect the extent of iron-related biofouling.

REFERENCES CITED

- Arbogast, B.F., 1996, Analytical methods for Mineral Resource Surveys Program: U.S. Geological Survey Open-File Report 96-525, 248 p.
- Aronson, D.A., Lindner, J.B., and Katz, B.G., 1983, Geohydrology of the Meadowbrook artificial-recharge site at East Meadow, Nassau County, New York: U.S. Geological Survey Water-Resources Investigations Report 82-4084, 44 p.
- Brown, C.J., 1998, Effects of geochemical and microbial reactions on iron and other redox-related constituents in the Magothy aquifer, Long Island, New York: Stony Brook, New York, State University of New York at Stony Brook, Ph.D. Dissertation, 163 p.
- Brown, C.J., and Schoonen, M.A.A., 1994, Iron reactions in the Magothy and upper glacial aquifers of Suffolk County, Long Island, New York, in *Geology of Long Island and Metropolitan New York*, April 23, 1994, Programs with Abstracts: Stony Brook, New York, Long Island Geologists, p. 1-7.
- Brown, C.J., Coates, J.D., and Schoonen, M.A.A., 1999a, Localized sulfate-reducing zones in the Magothy aquifer, Suffolk County, New York: *Ground Water*, v. 37, no. 4, p. 505-515.
- Brown, C.J., Schoonen, M.A.A., and Coates, J.D., 1999b, TEAP distribution and geochemical modeling of redox-active constituents in the Magothy aquifer, Long Island, New York (abst.), in 4th International Symposium on Subsurface Microbiology, August 22-27, 1999, Program and Abstracts: Vail, Colo., p. 42.
- Buxton, H.T., Soren, Julian, Posner, Alex, and Shernoff, P.K., 1981, Reconnaissance of the ground-water resources of Kings and Queens Counties, New York: U.S. Geological Survey Open-File Report 81-1186, 64 p.
- Caccavo, Jr., Frank, 1999, Bacterial iron mineral respiration—a natural strategy for enhanced bioavailability [abst.], in 4th International Symposium on Subsurface Microbiology, August 22-27, 1999, Program and Abstracts: Vail, Colo., p. 41.
- Canfield, D.E., Raiswell, Robert, and Bottrell, Simon, 1992, The reactivity of sedimentary iron minerals toward sulfide: *American Journal of Science*, v. 292, p. 659-683.

- Chapelle, F.H., 1993, Ground-water microbiology and geochemistry: New York, John Wiley, 424 p.
- Chukhrov, F.V., Zvyagin, B.B., Ermilova, L.P., and Gorshkov, 1973, New data on iron oxides in the weathering zone, in J.M. Serratos (ed.), Proceedings of the International Clay Conference: Madrid [Spain], Division de Ciencias C.S.I.C., p. 333-341.
- Coleman, M.L., Hedrick, D.B., Lovley, D.R., White, D.C., and Pye, Kenneth, 1993, Reduction of Fe(III) in sediments by sulphate-reducing bacteria: Letters to Nature, v. 361, p. 436-438.
- Creameans, D.L., Darmody, R.G., and Jansen, I.J., 1987, SEM analysis of weathered grains—pretreatment effects: Geology, v. 15, p. 401-404.
- Deer, W.A., Howie, R.A., and Zussman, Jack, 1978, An introduction to the rock-forming minerals: London [U.K.], Longman Group Limited, 528 p.
- Doriski, T.P., and Wilde-Katz, Franceska, 1983, Geology of the “20-foot” clay and Gardiners Clay in southern Nassau and southwestern Suffolk Counties, Long Island, New York: U.S. Geological Survey Water-Resources Investigations Report 82-4056, 17 p.
- Dryden, Lincoln, and Dryden, Clarissa, 1946, Comparative rates of weathering of some common heavy minerals: Journal of Sedimentary Petrology, v. 16, no. 3, p. 91-96.
- _____, 1956, Atlantic Coastal Plain heavy minerals—a speculative summary: Mexico, 20th International Geology Congress, Preprint, 18 p.
- Faust, G.T., 1963, Physical properties and mineralogy of selected samples of the sediments from the vicinity of the Brookhaven National Laboratory, Long Island, New York: U.S. Geological Survey Bulletin 1156-B, 135 p.
- Foord, E.E., Parrott, W.R., and Ritter, D.F., 1970, Definition of possible stratigraphic units in north central Long Island, New York, based on detailed examination of selected well cores: Journal of Sedimentary Petrology, v. 40, no. 1, p. 194-204.
- Groot, J.J., and Glass, H.D., 1960, Some aspects of the mineralogy of the northern Atlantic Coastal Plain, in Swineford, Ada (ed), Seventh National Conference on Clays and Clay Minerals: Washington, D.C., Pergamon Press, p. 271-284.
- Jensen, H.M., and Soren, Julian, 1971, Hydrogeologic data from selected wells and test holes in Suffolk County, Long Island, New York: Suffolk County Department Environmental Control, Long Island Water Resources Bulletin 3, 35 p.
- Krulik, R.K., and Koszalka, E.J., 1983, Geologic reconnaissance of an extensive clay unit in north-central Suffolk County, Long Island, New York: U.S. Geological Survey Water-Resources Investigations Report 82-4075, 9 p.
- Liebling, R.S., and Scherp, H.S., 1975, Stratigraphic importance of chlorite in the Cretaceous Raritan Formation: Geological Society of America Bulletin, v. 86, p. 925-928.
- Lonnie, T.P., 1982, Mineralogical and chemical comparison of marine, nonmarine, and transitional clay beds on the south shore of Long Island, New York: Journal of Sedimentary Petrology, v. 52, no. 2, p. 529-536.
- Lovley, D.R., 1987, Organic matter mineralization with the reduction of ferric iron—a review: Geomicrobiology Journal, v. 5, no. 3/4, p. 375-399.
- Lovley, D.R., and Phillips, E.J.P., 1986a, Availability of ferric iron for microbial reduction in bottom sediments of the freshwater tidal Potomac River: Applied and Environmental Microbiology, v. 52, p. 751-757.
- _____, 1986b, Organic matter mineralization with the reduction of ferric iron in anaerobic sediments: Applied Environmental Microbiology, v. 51, p. 683-689.
- Markewicz, F.J., Parillo, D.G., and Johnson, M.E., 1958, The titanium sand of southern New Jersey: Mining Engineering, v. 10, no. 1, p. 54-55.
- McClymonds, N.E., and Franke, O.L., 1972, Water-transmitting properties of aquifers on Long Island, New York: U.S. Geological Survey Professional Paper 627-E, 24 p.
- McKibben, M.A., and Barnes, H.L., 1986, Oxidation of pyrite in low temperature acidic solutions—rate laws and surface textures: Geochimica et Cosmochimica Acta, v. 50, p. 1509-1520.
- Moses, C. O., Nordstrom, D. K., Herman, J. S., and Mills, A. L., 1987, Aqueous pyrite oxidation by dissolved oxygen and ferric iron: Geochimica et Cosmochimica Acta, v. 51, p. 1561-1571.
- Murowchick, J.B., and Barnes, H.L., 1986, Marcasite precipitation from hydrothermal solutions: Geochimica et Cosmochimica Acta, v. 50, p. 2615-2630.
- Owens, J.P., Minard, J.P., Wiesnet, D.R., and Markewicz, F.J., 1960, Concentrations of “ilmeneite” in the Miocene and post-Miocene formations near Trenton, New Jersey: U.S. Geological Survey Professional Paper 400-B, p. B57-B59.
- Pearson, F.J., Jr., and Friedman, Irving, 1970, Sources of dissolved carbonate in an aquifer free of carbonate minerals: Water Resources Research, v. 6, no. 6, p. 1775-1781.
- Perlmutter, N.M., and Todd, Ruth, 1965, Correlation and Foraminifera of the Monmouth Group (Upper Cretaceous) Long Island, New York: U.S. Geological Survey Professional Paper 483-I, 24 p.
- Raiswell, Robert, 1982, Pyrite texture, isotopic composition and availability of iron: American Journal of Science, v. 282, p. 1244-1263.
- Rickard, David, Schoonen, M.A.A., and Luther, III, G.W., 1995, Chapter 9—Chemistry of iron sulfides in

- sedimentary environments, in Vairavamurthy, M.A., and Schoonen, M.A.A., (eds.), *Geochemical transformations of sedimentary sulfur*: Washington, D.C., American Chemical Society, p. 168-193.
- Rittenhouse, G., 1943, Transportation and deposition of heavy minerals: *Geological Society of America Bulletin*, v. 54, p. 1725-1780.
- Schoonen, M.A.A., and Barnes, H.L., 1991. Reactions forming pyrite and marcasite from solution—I, Nucleation of FeS₂ below 100°C: *Geochimica et Cosmochimica Acta*, v. 55, p. 1495-1504.
- Scorca, M.P., Reilly, T.E., and Franke, O.L., 1995, Selected hydrogeologic and water-quality data from Jones Beach Island, Long Island, New York: U.S. Geological Survey Water-Resources Investigations Report 92-4171, 21 p.
- Smolensky, D.A., Buxton, H.T., and Shernoff, P.K., 1989, Hydrologic framework of Long Island, New York: U.S. Geological Survey Hydrologic Investigations Atlas HA-709, 3 sheets, scale 1:250,000.
- Soren, Julian, 1971, Results of subsurface exploration in the mid-island area of western Suffolk County, Long Island, New York: Suffolk County Water Authority, Long Island Water Resources Bulletin 1, 60 p.
- Suter, Russell, de Laguna, Wallace, and Perlmutter, N.M., 1949, Mapping of geologic formations and aquifers of Long Island, New York: New York State Water Power and Control Commission Bulletin GW-18, 212 p.
- Walter, D.A., 1997, Geochemistry and microbiology of iron-related well-screen encrustation and aquifer biofouling in Suffolk County, Long Island, New York: U.S. Geological Survey Water-Resources Investigations Report 97-4032, 37 p.
- Wolff, R.G., 1967, X-ray and chemical study of weathering glauconite: *The American Mineralogist*, v. 52, p. 1129-1138.